

SECTION 1

INTRODUCTION

Natural attenuation processes (biodegradation, dispersion, sorption, volatilization) affect the fate and transport of chlorinated solvents in all hydrologic systems. When these processes are shown to be capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives, they may be selected alone or in combination with other more active remedies as the preferred remedial alternative. Monitored Natural Attenuation (MNA) is a term that refers specifically to the use of natural attenuation processes as part of overall site remediation. The United States Environmental Protection Agency (U.S. EPA) defines monitored natural attenuation as (OSWER Directive 9200.4-17, 1997):

The term “monitored natural attenuation,” as used in this Directive, refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to other methods. The “natural attenuation processes” that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and ground water. These in-situ processes include, biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants.

Monitored natural attenuation is appropriate as a remedial approach only when it can be demonstrated capable of achieving a site’s remedial objectives within a time frame that is reasonable compared to that offered by other methods and where it meets the applicable remedy selection program for a particular OSWER program. EPA, therefore, expects that monitored natural attenuation typically will be used in conjunction with active remediation measures (e.g., source control), or as a follow-up to active remediation measures that have already been implemented.

The intent of this document is to present a technical protocol for data collection and analysis to evaluate monitored natural attenuation through biological processes for remediating ground water contaminated with mixtures of fuels and chlorinated aliphatic hydrocarbons. This document focuses on technical issues and is not intended to address policy considerations or specific regulatory or statutory requirements. In addition, this document does not provide comprehensive guidance on overall site characterization or long-term monitoring of MNA remedies. Users of this protocol should realize that different Federal and State remedial programs may have somewhat different remedial objectives. For example, the CERCLA and RCRA Corrective Action programs generally require that remedial actions: 1) prevent exposure to contaminated ground water, above acceptable risk levels; 2) minimize further migration of the plume; 3) minimize further migration of contaminants from source materials; and 4) restore the plume to cleanup levels appropriate for current or future beneficial uses, to the extent practicable. Achieving such objectives could often require that MNA be used in conjunction with other “active” remedial methods. For other cleanup programs, remedial objectives may be focused on preventing exposures above acceptable levels. Therefore, it is imperative that users of this document be aware of and understand the Federal and

State statutory and regulatory requirements, as well as policy considerations that apply to a specific site for which this protocol will be used to evaluate MNA as a remedial option. As a general practice (i.e., not just pertaining to this protocol), individuals responsible for evaluating remedial alternatives should interact with the overseeing regulatory agency to identify likely characterization and cleanup objectives for a particular site prior to investing significant resources. The policy framework within which MNA should be considered for Federal cleanup programs is described in the November 1997 EPA Directive titled, “Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites” (Directive No. 9200.4-17).

This protocol is designed to evaluate the fate in ground water of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons. Because documentation of natural attenuation requires detailed site characterization, the data collected under this protocol can be used to compare the relative effectiveness of other remedial options and natural attenuation. This protocol should be used to evaluate whether MNA by itself or in conjunction with other remedial technologies is sufficient to achieve site-specific remedial objectives. In evaluating the appropriateness of MNA, the user of this protocol should consider both existing exposure pathways, as well as exposure pathways arising from potential future uses of the ground water.

This protocol is aimed at improving the characterization process for sites at which a remedy involving monitored natural attenuation is being considered. It contains methods and recommended strategies for completing the remedial investigation process. Emphasis is placed on developing a more complete understanding of the site through the conceptual site model process, early pathways analysis, and evaluation of remedial processes to include MNA. Understanding the contaminant flow field in the subsurface is essential for a technically justified evaluation of an MNA remedial option; therefore, use of this protocol is not appropriate for evaluating MNA at sites where the contaminant flow field cannot be determined with an acceptable degree of certainty (e.g., complex fractured bedrock, karst aquifers).

In practice, natural attenuation also is referred to by several other names, such as intrinsic remediation, intrinsic bioremediation, natural restoration, or passive bioremediation. The goal of any site characterization effort is to understand the fate and transport of the contaminants of concern over time in order to assess any current or potential threat to human health or the environment. Natural attenuation processes, such as biodegradation, can often be dominant factors in the fate and transport of contaminants. Thus, consideration and quantification of natural attenuation is essential to a more thorough understanding of contaminant fate and transport.

1.1 APPROPRIATE APPLICATION ON NATURAL ATTENUATION

The intended audience for this document includes Project Managers and their contractors, scientists, consultants, regulatory personnel, and others charged with remediating ground water contaminated with chlorinated aliphatic hydrocarbons or mixtures of fuel hydrocarbons and chlorinated aliphatic hydrocarbons. This protocol is intended to be used within the established regulatory framework appropriate for selection of a remedy at a particular hazardous waste site (e.g., the nine-criteria analysis used to evaluate remedial alternatives in the CERCLA remedy selection process). It is not the intent of this document to replace existing U.S. EPA or state-specific guidance on conducting remedial investigations.

The EPA does not consider monitored natural attenuation to be a default or presumptive remedy at any contaminated site (OSWER Directive 9200.4-17, 1997), as its applicability is highly variable from site to site. In order for MNA to be selected as a remedy, site-specific determinations

will always have to be made to ensure that natural attenuation is sufficiently protective of human health and the environment.

Natural attenuation in ground-water systems results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism, although abiotic destruction of some compounds does occur. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization. The natural attenuation of fuel hydrocarbons is described in the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater*, published by the Air Force Center for Environmental Excellence (AFCEE) (Wiedemeier *et al.*, 1995d). This document differs from the technical protocol for intrinsic remediation of fuel hydrocarbons because it focuses on the individual processes of chlorinated aliphatic hydrocarbon biodegradation which are fundamentally different from the processes involved in the biodegradation of fuel hydrocarbons.

For example, biodegradation of fuel hydrocarbons, especially benzene, toluene, ethylbenzene, and xylenes (BTEX), is mainly limited by electron acceptor availability, and generally will proceed until all of the contaminants biochemically accessible to the microbes are destroyed. In the experience of the authors, there appears to be an adequate supply of electron acceptors in most, if not all, hydrogeologic environments. On the other hand, the more highly chlorinated solvents such as perchloroethene (PCE) and trichloroethene (TCE) typically are biodegraded under natural conditions via reductive dechlorination, a process that requires both electron acceptors (the chlorinated aliphatic hydrocarbons) and an adequate supply of electron donors. Electron donors include fuel hydrocarbons or other types of anthropogenic carbon (e.g., landfill leachate) or natural organic carbon. If the subsurface environment is depleted of electron donors before the chlorinated aliphatic hydrocarbons are removed, biological reductive dechlorination will cease, and natural attenuation may no longer be protective of human health and the environment. This is the most significant difference between the processes of fuel hydrocarbon and chlorinated aliphatic hydrocarbon biodegradation.

For this reason, it is more difficult to predict the long-term behavior of chlorinated aliphatic hydrocarbon plumes than fuel hydrocarbon plumes. Thus, it is important to have a good understanding of the important natural attenuation mechanisms. Data collection should include all pertinent parameters to evaluate the efficacy of natural attenuation. In addition to having a better understanding of the processes of advection, dispersion, dilution from recharge, and sorption, it is necessary to better quantify biodegradation. This requires an understanding of the interactions between chlorinated aliphatic hydrocarbons, anthropogenic or natural carbon, and inorganic electron acceptors at the site. Detailed site characterization is required to adequately document and understand these processes. The long-term monitoring strategy should consider the possibility that the behavior of a plume may change over time and monitor for the continued availability of a carbon source to support reductive dechlorination.

An understanding of the attenuation mechanisms is also important to characterizing exposure pathways. After ground water plumes come to steady state, sorption can no longer be an important attenuation mechanism. The most important mechanisms will be biotransformation, discharge through advective flow, and volatilization. As an example, Martin and Imbrigiotta (1994) calibrated a detailed transport and fate model to a release of pure TCE at Picatinny Arsenal, in New Jersey. The plume was at steady state or declining. Ten years after surface spills ceased, leaching of contaminants from subsurface DNAPLs and desorption from fine-grained layers were the only processes identified that continued to contribute TCE to ground water. Desorption of TCE occurred

at a rate of 15 to 85 mg/second. Anaerobic biotransformation consumed TCE at a rate of up to 30 mg/second, advective flow and discharge of TCE to surface water accounted for up to 2 mg/second, and volatilization of TCE accounted for 0.1 mg/second. In this case, recharge of uncontaminated water drove the plume below the water table, which minimized the opportunity for volatilization to the unsaturated zone. As a result, discharge to surface water was the only important exposure pathway. Volatilization will be more important at sites that do not have significant recharge to the water table aquifer, or that have NAPLs at the water table that contain chlorinated organic compounds.

Chlorinated solvents are released into the subsurface as either aqueous-phase or nonaqueous phase liquids. Typical solvent releases include nonaqueous phase relatively pure solvents that are more dense than water and aqueous rinseates. Additionally, a release may occur as a mixture of fuel hydrocarbons or sludges and chlorinated aliphatic hydrocarbons which, depending on the relative proportion of each compound group, may be more or less dense than water. If the NAPL is more dense than water, the material is referred to as a “dense nonaqueous-phase liquid,” or DNAPL. If the NAPL is less dense than water the material is referred to as a “light nonaqueous-phase liquid,” or LNAPL. Contaminant sources generally consist of chlorinated solvents present as mobile NAPL (NAPL occurring at sufficiently high saturations to drain under the influence of gravity into a well) and residual NAPL (NAPL occurring at immobile, residual saturations that are unable to drain into a well by gravity). In general, the greatest mass of contaminant is associated with these NAPL source areas, not with the aqueous phase.

When released at the surface, NAPLs move downward under the force of gravity and tend to follow preferential pathways such as along the surface of sloping fine-grained layers or through fractures in soil or rock. Large NAPL releases can extend laterally much farther from the release point than would otherwise be expected, and large DNAPL releases can sink to greater depths than expected by following preferential flow paths. Thus, the relative volume of the release and potential migration pathways should be considered when developing the conceptual model for the distribution of NAPL in the subsurface.

As water moves through NAPL areas (recharge in the vadose zone or ground water flow in an aquifer), the more soluble constituents partition into the water to generate a plume of dissolved contamination and the more volatile contaminants partition to the vapor phase. After surface releases have stopped, NAPLs remaining in the subsurface tend to “weather” over time as volatile and soluble components are depleted from NAPL surfaces. Even considering this “weathering” effect, subsurface NAPLS continue to be a source of contaminants to ground water for a very long time. For this reason, identification and delineation of subsurface zones containing residual or free-phase NAPL is an important aspect of the site conceptual model to be developed for evaluating MNA or other remediation methods.

Removal, treatment or containment of NAPLs may be necessary for MNA to be a viable remedial option or to decrease the time needed for natural processes to attain site-specific remediation objectives. In cases where removal of mobile NAPL is feasible, it is desirable to remove this source material and decrease the time required to reach cleanup objectives. Where removal or treatment of NAPL is not practical, source containment may be practicable and necessary for MNA to be a viable remedial option.

1.2 ADVANTAGES AND DISADVANTAGES

In comparison to engineered remediation technologies, remedies relying on monitored natural attenuation have the following advantages and disadvantages, as identified in OSWER Directive

9200.4-17, dated November 1997. (Note that this is an interim, not a final, Directive which was released by EPA for use. Readers are cautioned to consult the final version of this Directive when it becomes available.)

The **advantages** of monitored natural attenuation (MNA) remedies are:

- *As with any in situ process, generation of lesser volume of remediation wastes reduced potential for cross-media transfer of contaminants commonly associated with ex situ treatment, and reduced risk of human exposure to contaminated media;*
- *Less intrusion as few surface structures are required;*
- *Potential for application to all or part of a given site, depending on site conditions and cleanup objectives;*
- *Use in conjunction with, or as a follow-up to, other (active) remedial measures; and*
- *Lower overall remediation costs than those associated with active remediation.*

The **potential disadvantages** of monitored natural attenuation (MNA) include:

- *Longer time frames may be required to achieve remediation objectives, compared to active remediation;*
- *Site characterization may be more complex and costly;*
- *Toxicity of transformation products may exceed that of the parent compound;*
- *Long-term monitoring will generally be necessary;*
- *Institutional controls may be necessary to ensure long-term protectiveness;*
- *Potential exists for continued contamination migration, and/or cross-media transfer of contaminants;*
- *Hydrologic and geochemical conditions amenable to natural attenuation are likely to change over time and could result in renewed mobility of previously stabilized contaminants, adversely impacting remedial effectiveness; and*
- *More extensive education and outreach efforts may be required in order to gain public acceptance of monitored natural attenuation.*

At some sites the same geochemical conditions and processes that lead to biodegradation of chlorinated solvents and petroleum hydrocarbons can chemically transform naturally occurring manganese, arsenic and other metals in the aquifer matrix, producing forms of these metals that are more mobile and/or more toxic than the original materials. A comprehensive assessment of risk at a hazardous waste site should include sampling and analysis for these metals.

This document describes (1) those processes that bring about natural attenuation, (2) the site characterization activities that may be performed to conduct a full-scale evaluation of natural attenuation, (3) mathematical modeling of natural attenuation using analytical or numerical solute fate and transport models, and (4) the post-modeling activities that should be completed to ensure successful evaluation and verification of remediation by natural attenuation. The objective is to quantify and provide defensible data to evaluate natural attenuation at sites where naturally occurring subsurface attenuation processes are capable of reducing dissolved chlorinated aliphatic hydrocarbon and/or fuel hydrocarbon concentrations to acceptable levels. A comment made by a member of the regulatory community summarizes what is required to successfully implement natural attenuation:

A regulator looks for the data necessary to determine that a proposed treatment technology, if properly installed and operated, will reduce the contaminant concentrations in the soil and water to legally mandated limits. In this sense, the use of biological treatment systems calls for the same level of investigation,

demonstration of effectiveness, and monitoring as any conventional [remediation] system (National Research Council, 1993).

When the rate of natural attenuation of site contaminants is sufficient to attain site-specific remediation objectives in a time period that is reasonable compared to other alternatives, MNA may be an appropriate remedy for the site. This document presents a technical course of action that allows converging lines of evidence to be used to scientifically document the occurrence of natural attenuation and quantify the rate at which it is occurring. Such a “weight-of-evidence” approach will greatly increase the likelihood of successfully implementing natural attenuation at sites where natural processes are restoring the environmental quality of ground water.

1.3 LINES OF EVIDENCE

The OSWER Directive 9200.4-17 (1997) identifies three lines of evidence that can be used to estimate natural attenuation of chlorinated aliphatic hydrocarbons, including:

- (1) *Historical ground water and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a ground water plume, decreasing concentrations should not be solely the result of plume migration. In the case of inorganic contaminants, the primary attenuating mechanism should also be understood.)*
- (2) *Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.*
- (3) *Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).*

The OSWER Directive provides the following guidance on interpreting the lines of evidence:

Unless EPA or the implementing state agency determines that historical data (Number 1 above) are of sufficient quality and duration to support a decision to use monitored natural attenuation, EPA expects that data characterizing the nature and rates of natural attenuation processes at the site (Number 2 above) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (Number 3 above) may also be necessary. In general, more supporting information may be required to demonstrate the efficacy of monitored natural attenuation at those sites with contaminants which do not readily degrade through biological processes (e.g., most non-petroleum compounds, inorganics), at sites with contaminants that transform into more toxic and/or mobile forms than the parent contaminant, or at sites where monitoring has been performed for a relatively short period of time. The amount and type of information needed for such a demonstration will depend upon a number of site-specific factors, such as the size and nature of the contamination problem, the proximity of receptors and the potential risk to those receptors, and other physical characteristics of the environmental setting (e.g., hydrogeology, ground cover, or climatic conditions).

The first line of evidence does not prove that contaminants are being destroyed. Reduction in contaminant concentration could be the result of advection, dispersion, dilution from recharge, sorption, and volatilization (i.e., the majority of apparent contaminant loss could be due to dilution). However, this line of evidence is critical for determining if any exposure pathways exist for current or potential future receptors.

In order to evaluate remediation by natural attenuation at most sites, the investigator will have to determine whether contaminant mass is being destroyed. This is done using either, or both, of the second or third lines of evidence. The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed, not just being diluted or sorbed to the aquifer matrix. For many contaminants, biodegradation is the most important process, but for certain contaminants nonbiological reactions are also important. The second line of evidence is divided into two components:

- Using chemical analytical data in mass balance calculations to show that decreases in contaminant and electron acceptor/donor concentrations can be directly correlated to increases in metabolic end products/daughter compounds. This evidence can be used to show that electron acceptor/donor concentrations in ground water are sufficient to facilitate degradation of dissolved contaminants. Solute fate and transport models can be used to aid mass balance calculations and to collate and present information on degradation.
- Using measured concentrations of contaminants and/or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

The biodegradation rate constants are used in conjunction with the other fate and transport parameters to predict contaminant concentrations and to assess risk at downgradient performance evaluation wells and within the area of the dissolved plume.

Microcosm studies may be necessary to physically demonstrate that natural attenuation is occurring. Microcosm studies can also be used to show that indigenous biota are capable of degrading site contaminants at a particular rate. Microcosm studies **for the purpose of developing rate constants** should only be undertaken when they are the only means available to obtain biodegradation rate estimates. There are two important categories of sites where it is difficult or impossible to extract rate constants from concentrations of contaminants in monitoring wells in the field. In some sites, important segments of the flow path to receptors are not accessible to monitoring because of landscape features (such as lakes or rivers) or property boundaries that preclude access to a site for monitoring. In other sites that are influenced by tides, or the stage of major rivers, or ground water extraction wells, the ground water plume trajectory changes so rapidly that it must be described in a statistical manner. A “snapshot” round of sampling cannot be used to infer the plume velocity in calculations of the rate of attenuation.

1.4 SITE CHARACTERIZATION

The OSWER Directive 9200.4-17 (1997) describes EPA requirements for adequate site characterization.

Decisions to employ monitored natural attenuation as a remedy or remedy component should be thoroughly and adequately supported with site-specific characterization data and analysis. In general, the level of site characterization necessary to support a comprehensive evaluation of natural attenuation is more detailed than that needed to support active remediation. Site characterizations for

natural attenuation generally warrant a quantitative understanding of source mass; ground water flow; contaminant phase distribution and partitioning between soil, ground water, and soil gas; rates of biological and non-biological transformation; and an understanding of how all of these factors are likely to vary with time. This information is generally necessary since contaminant behavior is governed by dynamic processes which must be well understood before natural attenuation can be appropriately applied at a site. Demonstrating the efficacy of this remediation approach likely will require analytical or numerical simulation of complex attenuation processes. Such analyses, which are critical to demonstrate natural attenuation's ability to meet remedial action objectives, generally require a detailed conceptual site model as a foundation.

*A conceptual site model is a three-dimensional representation that conveys what is known or suspected about contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual model provides the basis for assessing potential remedial technologies at the site. "Conceptual site model" is **not** synonymous with "computer model;" however, a computer model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions. Computer models, which simulate site processes mathematically, should in turn be based upon sound conceptual site models to provide meaningful information. Computer models typically require a lot of data, and the quality of the output from computer models is directly related to the quality of the input data. Because of the complexity of natural systems, models necessarily rely on simplifying assumptions that may or may not accurately represent the dynamics of the natural system.*

Site characterization should include collecting data to define (in three spatial dimensions over time) the nature and distribution of contamination sources as well as the extent of the ground water plume and its potential impacts on receptors. However, where monitored natural attenuation will be considered as a remedial approach, certain aspects of site characterization may require more detail or additional elements. For example, to assess the contributions of sorption, dilution, and dispersion to natural attenuation of contaminated ground water, a very detailed understanding of aquifer hydraulics, recharge and discharge areas and volumes, and chemical properties is required. Where biodegradation will be assessed, characterization also should include evaluation of the nutrients and electron donors and acceptors present in the ground water, the concentrations of co-metabolites and metabolic by-products, and perhaps specific analyses to identify the microbial populations present. The findings of these, and any other analyses pertinent to characterizing natural attenuation processes, should be incorporated into the conceptual model of contaminant fate and transport developed for the site.

Development of an adequate database during the iterative site characterization process is an important step in the documentation of natural attenuation. Site characterization should provide data on the location, nature, phase distribution, and extent of contaminant sources. Site characterization also should provide information on the location, extent, and concentrations of dissolved contamination; ground water geochemical data; geologic information on the type and distribution of subsurface materials; and hydrogeologic parameters such as hydraulic conductivity,

hydraulic gradients, and potential contaminant migration pathways to human or ecological receptor exposure points.

The data collected during site characterization can be used to simulate the fate and transport of contaminants in the subsurface. Such simulation allows prediction of the future extent and concentrations of the dissolved contaminant plume. Several types of models can be used to simulate dissolved contaminant transport and attenuation.

The natural attenuation modeling effort has five primary objectives:

- To evaluate whether MNA will be likely to attain site-specific remediation objectives in a time period that is reasonable compared to other alternatives;
- To predict the future extent and concentration of a dissolved contaminant plume by simulating the combined effects of contaminant loading, advection, dispersion, sorption, and biodegradation;
- To predict the most useful locations for ground-water monitoring;
- To assess the potential for downgradient receptors to be exposed to contaminant concentrations that exceed regulatory or risk-based levels intended to be protective of human health and the environment; and
- To provide technical support for remedial options using MNA during screening and detailed evaluation of remedial alternatives in a CERCLA Feasibility Study or RCRA Corrective Measures Study.

Upon completion of the fate and transport modeling effort, model predictions can be used to evaluate whether MNA is a viable remedial alternative for a given site. If the transport and fate models predict that natural attenuation is sufficient to attain site-specific remediation objectives and will be protective of human health and the environment, natural attenuation may be an appropriate remedy for the site. Model assumptions and results should be verified by data obtained from site characterization. If model assumptions and results are not verified by site data, MNA is not likely to be a viable option and should not be proposed as the remedy.

1.5 MONITORING

The Monitoring Program OSWER Directive on Monitored Natural Attenuation (9200.4-17) describes EPA expectations for performance monitoring.

Performance monitoring to evaluate remedy effectiveness and to ensure protection of human health and the environment is a critical element of all response actions. Performance monitoring is of even greater importance for monitored natural attenuation than for other types of remedies due to the longer remediation time frames, potential for ongoing contaminant migration, and other uncertainties associated with using monitored natural attenuation. This emphasis is underscored by EPA's reference to "monitored natural attenuation".

The monitoring program developed for each site should specify the location, frequency, and type of samples and measurements necessary to evaluate remedy performance as well as define the anticipated performance objectives of the remedy. In addition, all monitoring programs should be designed to accomplish the following:

- *Demonstrate that natural attenuation is occurring according to expectations;*
- *Identify any potentially toxic transformation products resulting from biodegradation;*
- *Determine if a plume is expanding (either downgradient, laterally or vertically);*
- *Ensure no impact to downgradient receptors;*
- *Detect new releases of contaminants to the environment that could impact the*

- effectiveness of the natural attenuation remedy;*
- *Demonstrate the efficacy of institutional controls that were put in place to protect potential receptors;*
- *Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes; and*
- *Verify attainment of cleanup objectives.*

Detection of changes will depend on the proper siting and construction of monitoring wells/points. Although the siting of monitoring wells is a concern for any remediation technology, it is of even greater concern with monitored natural attenuation because of the lack of engineering controls to control contaminant migration.

***Performance monitoring should continue as long as contamination remains above required cleanup levels.** Typically, monitoring is continued for a specified period (e.g., one to three years) after cleanup levels have been achieved to ensure that concentration levels are stable and remain below target levels. The institutional and financial mechanisms for maintaining the monitoring program should be clearly established in the remedy decision or other site documents, as appropriate.*

Natural attenuation is achieved when naturally occurring attenuation mechanisms, such as biodegradation, bring about a reduction in the total mass, toxicity, mobility, volume, or concentration of a contaminant dissolved in ground water. In some cases, natural attenuation processes will be capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives. However, at this time, the authors are not aware of any sites where natural attenuation alone has succeeded in restoring ground water contaminated with chlorinated aliphatic hydrocarbons to drinking water quality over the entire plume.

The material presented here was prepared through the joint effort between the Bioremediation Research Team at the Subsurface Protection and Remediation Division of U.S. EPA's National Risk Management Research Laboratory (NRMRL) in Ada, Oklahoma, and the U.S. Air Force Center for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, Texas, and Parsons Engineering Science, Inc. (Parsons ES). It is designed to facilitate proper evaluation of remedial alternatives including natural attenuation at large chlorinated aliphatic hydrocarbon-contaminated sites.

This information is the most current available at the time of this writing. The scientific knowledge and experience with natural attenuation of chlorinated solvents is growing rapidly and the authors expect that the process for evaluating natural attenuation of chlorinated solvents will continue to evolve.

This document contains three sections, including this introduction. Section 2 presents the protocol to be used to obtain scientific data to evaluate the natural attenuation option. Section 3 presents the references used in preparing this document. Appendix A describes the collection of site characterization data necessary to evaluate natural attenuation, and provides soil and ground-water sampling procedures and analytical protocols. Appendix B provides an in-depth discussion of the destructive and nondestructive mechanisms of natural attenuation. Appendix C covers data interpretation and pre-modeling calculations.